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The r_e Structure of Cyclopropane

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A long-standing controversy regarding the r_e structure of cyclopropane is resolved by performing high-level quantum chemical calculations and analyzing the experimental rotational constants for C_3H_6 and $C_3H_4D_2$ augmented by calculated vibrational corrections. For the latter, a least-squares fit yields the following set of parameters: r_e (CC) = 1.5030(10) Å, r_e(CH) = 1.0786(10) Å, and α_e(HCH) = 114.97(10)°, which compare favorably with both the pure computational result obtained at the CCSD(T)/cc-pVQZ level as well as an earlier estimate of the r_e structure of cyclopropane based on analysis of gas-phase electron diffraction data. Our results are in rather poor agreement with a structure based on a previous analysis of the rotational constants that used empirically estimated vibrational corrections.

I. Introduction

The knowledge of exact molecular geometries is an important prerequisite for the understanding of the electronic structure and chemical reactivity of molecules. An enormous amount of geometrical data for molecules has been determined by various experimental techniques ranging from spectroscopic (microwave, infrared, Raman, etc.) to diffraction methods (electron diffraction, X-ray diffraction, neutron diffraction, etc.).[1−6] These techniques yield structural information such as average nuclear positions in ground (or excited) vibrational state(s) of the molecule, thermally averaged values of distances and angles, or in the form of effective ground-state rotational constants that are related to the geometrical parameters of a molecule.[7] However, the derived molecular geometrical parameters (r_0, r_g, r_α, r_z, also r_s, r_m, r_a, r_v) are not directly comparable; some do not even possess physical significance. For many small molecules or molecules with high symmetry, however, it is possible to find (approximate) relationships between the various molecular geometries determined by experimental means and, thus, to derive from them equilibrium geometries r_e that are well-defined and also directly comparable to geometries calculated with reliable quantum chemical methods.[7,8]

Considering the wealth of structural data collected since the onset of structure determination in the 1920s, it is justified to say that reliable geometrical data are available for almost all common organic and inorganic compounds. Experimentally based r_e geometries are less frequent, but have also been reported for a large number of molecules. It is thus somewhat surprising that the equilibrium geometry of a prototype organic compound such as cyclopropane is still a matter of controversy. Early spectroscopic investigations by Jones and Stoicheff (1964)[9] as well as by Butcher and Jones (1973)[10] led to an (effective) r_0 geometry of cyclopropane [r_0(CC) = 1.512 Å, r_0(CH) = 1.083 Å, α_0(HCH) = 114.0°] that was based on the assumption that r_0(CH) − r_0(CD) = 0.002 Å. This geometry has been cited in many chemistry textbooks for years. Electron diffraction studies first carried out by Bastiansen, Fritsch, and Hedberg (1964)[11] and later repeated by Yamamoto, Nakata, Fukuyama, and Kuchitsu (YNFK, 1985)[12] led to an r_g geometry [r_g(CC) = 1.514 Å, r_g(CH) = 1.099 Å]. Using the harmonic force field reported by Spiekermann and co-workers[13] together with a simple diatomic approximation for the extrapolation to 0 K, YNFK also obtained the r_z geometry of cyclopropane [r_z(CC) = 1.5127 Å, r_z(CH) = 1.0840 Å, α_z(HCH) = 114.5°]. This geometry was later confirmed by Endo, Chang, and Hirota (ECH, 1987),[14] who measured the microwave spectrum of cyclopropane-1,1-d_2 and determined its rotational and centrifugal distortion constants. Using these data and published rotational constants for C_3H_6 (B_0, C_0) and C_3D_6 (B_0), ECH obtained an improved r_0 geometry of cyclopropane [r_0(CC) = 1.5153 Å, r_0(CH) = 1.0774 Å, α_0(HCH) = 115.57°, r_0(CH) − r_0(CD) = −0.0016 Å].[14] Their r_z geometry [r_z(CC) = 1.5157 Å, r_z(CH) = 1.0797 Å, α_z(HCH) = 115.47°, r_z(CH) − r_z(CD) = 0.0003 Å], although based on a different harmonic force field than that used by YNFK, turned out to agree with the r_z geometry of YNFK within estimated uncertainties. YNFK combined the information gained from gas-phase electron diffraction and various spectroscopic studies to derive the r_e geometry of cyclopropane. Their determination was based on the assumption that α_e(HCH) = α_z(HCH) and the use of effective CC and CH stretching anharmonicity constants obtained from rotational constants for the ν_{11} (CC stretching mode) vibrational state and that for the perdeuterated species.[12] Another r_e geometry was derived by ECH two years later from reported vibration−rotation constants considering just the CC and CH stretching cubic force constants

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as adjustable parameters.[14] Contrary to the close agreement between the r_z geometries obtained from electron diffraction and microwave measurements, the r_e geometries of ECH and YNFK differ by 0.01 Å in CC and CH bond lengths (1.510 vs 1.501 Å and 1.074 vs 1.083 Å) and 1.3° in the HCH angle (115.8 vs 114.5°), which is well outside the error bars given in the two investigations.[12,14]

The discrepancy between the two r_e geometries derived from electron diffraction and microwave measurements has to be seen in view of the important role the equilibrium geometry of cyclopropane plays in understanding the nature of the CC bond in organic compounds.[15] This role can be assessed if one compares the bond lengths of typical CC bonds such as the single bond in ethane, the double bond in ethylene, the triple bond in acetylene, and their analogues in the conjugated systems such as 1,3-butadiene, benzene, or 1,3-butadiyne. The CC bond in cyclopropane does not fit any of these categories since it is shorter than the CC single bond in ethane. The difference is estimated to be as large as 0.04 Å depending on which r_e geometry is used for the comparison. It has been shown that the CC bond in cyclopropane behaves chemically in many ways like the ethylene double bond; however, it is considerably longer than both the formal CC single bond in 1,3-butadiene (1.46 Å) and the CC double bond in ethene (1.34 Å).[15,16] Hence, the CC bond in cyclopropane represents a bond type of its own, which obtains its unique character by the strong bending of the bond.[17,18] The degree of bond bending, however, can only be properly assessed if the CC internuclear distance is known to within 0.002 Å. Knowledge of the exact r_e geometry of cyclopropane thus appears essential for understanding the unique electronic features of this molecule. Since the r_e determinations of YNFK[12] and ECH[14] are based on a number of assumptions, it is not clear which of these structures should be preferred. One could utilize published ab initio equilibrium geometries for cyclopropane to decide which of the two experimental r_e geometries is more reliable. In fact, a recent review on ab initio studies of cyclopropane tends to give higher credibility to the r_e structure of ECH, as CCSD(T) calculations with a polarized TZ basis lead to r_e parameters in better agreement with the ECH than the YNFK geometry.[18] However, such calculations do not necessarily provide a reliable estimate for the basis set limit and should be regarded with some care, as benchmark calculations on small molecules indicate that much larger basis sets with inclusion of higher angular momentum functions are needed to obtain sufficiently converged results for geometrical parameters in electron-correlated calculations.[19−21]

In this work, we follow a two-pronged strategy to resolve the controversy about the r_e structure of cyclopropane. First, the r_e geometry is calculated using coupled-cluster (CC) methods (for recent reviews, see ref 22) together with large, correlation-consistent basis sets. Since most of the correlation effects in cyclopropane should be covered at the CC level—in particular when triple excitations are included—such calculations should provide bond distances with an accuracy of about 0.002 Å.[19−21,23,24]

Second, we reanalyze the experimental microwave data using calculated vibrational corrections for the rotational constants, thus addressing the weak point of the original analysis in ref 14. While experimental determination of vibration−rotation interaction constants is tedious and most often incomplete, quantum chemical calculations of these parameters have turned out to be useful and have enabled the determination of a number of accurate r_e structures with an accuracy of 0.001 Å on the basis of experimental rotational constants (see, for example, refs 23−27). Most important, our approach allows a consistency check, as both the purely theoretical structure and the empirical structure based on experimental rotational constants should agree within their error bars.

II. Computational Approach

A. Equilibrium Geometries. As a large number of computational studies has shown, the coupled-cluster singles and doubles (CCSD) approach[28] augmented by a perturbative treatment of triple excitations (CCSD(T))[29] yields near quantitative accuracy in many cases, provided sufficiently large basis sets are used.[22] The choice of a systematic series of basis sets is facilitated by Dunning's hierarchy of correlation-consistent sets denoted by cc-pVXZ with X = D, T, Q, ...[30] For geometries, it has been demonstrated that CCSD(T)/cc-pVQZ calculations typically yield results with a residual error of 0.002−0.003 Å for bond distances and a few tenths of a degree for bond angles[20] when compared to reliable r_e structures. While these conclusions are largely based on a systematic study for a range of small molecules,[20] the findings have been also verified for larger systems such as dioxirane[23] and propadienylidene.[24]

On the basis of this experience, we have carried out geometry optimizations for cyclopropane at the CCSD(T) level using Dunning's cc-pVXZ sets[30] with X = D [3s2p1d/2s1p], T [4s3p2d1f/3s2p1d], and Q [5s4p3d2f1g/4s3p2d1f]. While the CCSD(T)/cc-pVQZ calculations (345 basis functions) provide our best theoretical estimate for the r_e structure of cyclopropane, calculations with the smaller cc-pVDZ (72 basis functions) and cc-pVTZ (174 basis functions) sets provide information about basis set convergence.[31] In the same spirit, additional calculations at MBPT(2), SDQ-MBPT(4),[32] and CCSD levels[28] have been performed to monitor convergence of the electron correlation treatment.

The geometry calculations with the smaller basis sets were carried out using analytic gradients,[33] while disk space limitations forced those with the larger cc-pVQZ set to be based on numerically evaluated gradients. The geometry calculations were converged in such a manner that all distances are accurate to better than 0.0001 Å.

B. Vibrational Corrections. Vibrational corrections to rotational constants are usually given in the following form

$$B_\upsilon = B_e - \sum_r \alpha_r^B\left(\upsilon_r + \frac{1}{2}\right) + ... \qquad (1)$$

with B_e as the equilibrium value (the rotational constant for the molecule at the mininum on the Born−Oppenheimer potential energy surface) and B_υ the rotational constants for the vibrational state υ. The sum in eq 1 runs over all normal modes r;[35] α_r^B are the vibration−rotation interaction constants and υ_r the corresponding quantum numbers. The vibration−rotation interaction constants can in principle be obtained from rotationally resolved vibrational spectra, but the analysis is usually complicated. Furthermore, in most cases only a few selected values can be determined, and the full set (that is required for the computation of vibrational corrections to B) is rarely available.

An expression for the vibration−rotation interaction constants can be derived using perturbation theory starting from a rigid-rotator harmonic-oscillator Hamiltonian. In second order, one obtains[34,36]

$$\alpha_r^B = -\frac{2B_e^2}{\omega_r}\left[\sum_{\xi} \frac{3(a_r^{(b\xi)})^2}{4I_\xi} + \sum_r (\zeta_{r,s}^{(b)})^2 \frac{(3\omega_r^2 + \omega_s^2)}{\omega_r^2 - \omega_s^2} + \pi\left(\frac{c}{h}\right)^{1/2} \sum_s \phi_{rrs} a_s^{(bb)} \left(\frac{\omega_r}{\omega_s^{3/2}}\right)\right] \quad (2)$$

with ω_r as the harmonic frequency of the rth mode, I_ξ the ξth principal components of the inertia tensor at the equilibrium geometry, and $a_r^{(ab)}$ the corresponding derivative of I_{ab} with respect to the normal coordinate Q_r. Furthermore, $\zeta_{r,s}^{(b)}$ denotes the Coriolis matrices and ϕ_{rst} the cubic force constants defined in terms of dimensionless normal coordinates (for the exact definition, see for example, ref 34).

The three terms in eq 2 are interpreted in the following way: the first arises from the quadratic dependence of B on the normal coordinate, thus causing already in the harmonic approximation a change in B due to the mean-square displacement of Q_r^2, the second term is due to Coriolis interactions between normal modes Q_r and Q_s, and the third term arises from a shift in the mean-square displacement of the normal mode Q_r due to anharmonicity. The first and second contributions are easily obtained from the results of a harmonic force field (second derivative) calculation, while the third term is computationally more demanding and requires determination of the cubic force field. As all three contributions are generally of comparable importance, accurate prediction of vibration–rotation interaction constants necessitates the computation of anharmonic force constants and therefore are rather costly.

Anharmonic effects are also essential for the direct quantum chemical computation of the parameters extracted from the electron diffraction data. The mean internuclear distances r_g and the mean distance between nuclear positions r_α (see ref 37 for definitions) can be written in terms of the normal coordinate representation[38] as

$$\begin{aligned} r_g &= r_e + \sum_s \gamma_s \langle Q_s \rangle + \frac{1}{2}\sum_{st} \gamma_{st} \langle Q_s Q_t \rangle + \ldots \\ &\approx r_e + \sum_s \gamma_s \langle Q_s \rangle + \frac{1}{2}\sum_s \gamma_{ss} \langle Q_s^2 \rangle \end{aligned} \quad (3)$$

and

$$r_\alpha = r_e + \sum_s \gamma_s \langle Q_s \rangle \quad (4)$$

where γ_s and γ_{st} are the first and second derivatives of the internuclear distances with respect to the corresponding normal coordinates, evaluated at the equilibrium geometry. If temperature effects are ignored, these quantities are easily computed using for $\langle Q_r^2 \rangle$ the expression obtained in the harmonic-oscillator approximation

$$\langle {Q_r}^2 \rangle = \frac{\hbar}{4\pi c \omega_r} \quad (5)$$

and the formula obtained in second-order perturbation theory for $\langle Q_r \rangle$

$$\langle Q_r \rangle = -\left(\frac{\hbar}{2\pi c \omega_r^3}\right)^{1/2} \sum_s \phi_{rss} \quad (6)$$

TABLE 1: Calculated Geometrical Parameters (Bond Distances in Å, Angles in Deg) for Cyclopropane (C_3H_6)

	r(CC)	r(CH)	α(HCH)
HF-SCF/cc-pVTZ	1.4959	1.0733	114.20
MBPT(2)/cc-pVTZ	1.4984	1.0744	115.06
SDQ-MBPT(4)/cc-pVTZ	1.4996	1.0753	114.72
CCSD/cc-pVTZ	1.4996	1.0754	114.74
CCSD(T)/cc-pVDZ	1.5196	1.0958	114.66
CCSD(T)/cc-pVTZ	1.5040	1.0770	114.89
CCSD(T)/cc-pVQZ	1.5019	1.0781	114.81

Note that use of eqs 5 and 6 corresponds to averages over the vibrational ground state, in which r_α by definition is equal to r_z.[37] Hence, our calculated values may be compared directly with the r_g and r_z values reported in refs 12 and 14.

While the harmonic force field calculations have been carried out analytically using our recent implementation of analytic CC/MBPT second derivatives,[39] the required parts of the cubic force field have been obtained by numerical differentiation of analytically evaluated second derivatives with respect to the normal coordinates (for details, see ref 23). Since vibrational corrections to the rotational constants are only required for C_3H_6 and $C_3H_4D_2$, all force constants needed for the analysis can be obtained by taking displacements along the totally symmetric normal modes within C_{2v} symmetry, the molecular point group of the deuterated isotopomer. Using double-sided numerical differentiation, 14 second-derivative calculations are required. Furthermore, since the cubic force field calculations are computationally rather demanding, these calculations have been performed at the SDQ-MBPT(4)/cc-pVTZ level. Previous experience suggests that this is a good compromise between accuracy and computational cost.[23,24]

To obtain more accurate theoretical values for r_g and r_z, we combine our best theoretical r_e parameters (obtained at the CCSD(T)/cc-pVQZ level) with vibrational corrections obtained at the SDQ-MBPT(4)/cc-pVTZ level. This is justified, as the vibrational corrections are generally small and the main error in the SDQ-MBPT(4)/cc-pVTZ values for r_g and r_z is due to inaccuracies in the calculated r_e values.

C. Analysis of Experimental Rotational Constants. To obtain an accurate r_e structure from the experimental rotational constants for C_3H_6 and $C_3H_4D_2$, the following procedure has been applied. First, the experimental rotational constants (B_0 values) are corrected according to eq 1 using computed vibration–rotation interaction constants in order to obtain the corresponding equilibrium values (B_e values). Second, the r_e parameters are determined by a least-squares fit of the structural parameters to the rotational constants. For the fit, either just the three rotational constants for $C_3H_4D_2$ or the three rotational constants for $C_3H_4D_2$ together with the reported B value for C_3H_6 are used. Other reported rotational constants (C_0 for C_3H_6 and B_0 for C_3D_6) do not appear particularly reliable; i.e., the reported error bars are quite large,[14] so we decided to exclude them from the analysis.

III. Results and Discussion

Table 1 compares the computed geometries obtained at the various levels of theory. We note a rather smooth convergence with respect to basis set and electron correlation. Our best calculation—that at the CCSD(T)/cc-pVQZ level—yields 1.5019

TABLE 2: Calculated and Experimental r_e, r_g, and r_z Distances (in Å) for Cyclopropane

	r(CC)			r(CH)		
	r_e	r_g	r_z	r_e	r_g	r_z
SDQ-MBPT(4)/cc-pVTZ	1.4996	1.5098	1.5089	1.0753	1.0958	1.0811
CCSD(T)/cc-pVQZ[a]	1.5019	1.5120	1.5111	1.0781	1.0986	1.0838
experiment[b]	1.501(4)	1.5139(12)	1.5127(12)	1.083(5)	1.0991(20)	1.0840(20)
experiment[c]	1.5101(23)		1.5157(69)	1.0742(29)		1.080(10)

[a] Vibrational corrections obtained at the SDQ-MBPT(4)/cc-pVTZ level. [b] Obtained from electron diffraction data.[12] [c] Obtained from rotational constants.[14]

TABLE 3: r_e Structure (Bond Distances in Å, Angles in deg) of Cyclopropane As Obtained from the Analysis of Experimental Data in Comparison with Calculations

	ref 14[a]	ref 12[b]	this work[c]	calcn[d]
r(CC)	1.5101(23)	1.501(4)	1.5030(10)	1.5019
r(CH)	1.0742(29)	1.083(5)	1.0786(10)	1.0781
⟨(HCH)	115.85(33)	114.5(9)	114.97(10)	114.81

[a] Obtained from rotational constants (see ref 14 for details). [b] Obtained from electron diffraction data (see ref 12 for details). [c] Obtained from analysis of rotational constants[14] with calculated vibration−rotation interaction constants (SDQ-MBPT(4)/cc-pVTZ level). [d] CCSD(T)/cc-pVQZ calculations.

Å for the CC distance, 1.0781 Å for the CH distance, and 114.81° for the HCH bond angle. The computed CC distance (with an estimated residual error of about 0.002 Å) is more consistent with that derived from electron diffraction [r_e(CC) = 1.501(4) Å] than with the distance of 1.5101(23) Å determined in ref 14 from rotational constants. The computational results are clearly outside the quoted error bars for the latter value.

Table 2 summarizes and compares our computed r_e, r_z, and r_g values with those reported in refs 12 and 14. Vibrational effects on the bond distances amount to about 0.01 Å for the CC distance and 0.02 Å for the CH distance. Good agreement with experiment is obtained when r_g and r_z distances are compared. Agreement with the electron diffraction data appears to be slightly better, although the r_z distances derived from the rotational constants are also consistent with our calculations: differences are noted only for the r_e parameters as discussed earlier. From the comparison in Table 2, it is clear that the main source of discrepancy is the vibrational corrections. For the CC distance, we obtain for $\delta r = r_z - r_e$ a value of 0.009 Å compared to 0.006 Å in ref 14. The differences are artificially magnified by the fact that the r_z value reported in ref 14 for the CC distance appears to be slightly too large (though correct within the given error bars) and the value for the CH distance somewhat too short.

Table 3 reports the r_e structure obtained from analysis of the experimental rotational constants together with the computed vibrational corrections. In addition, we compare our r_e structure with previous estimates as well as results of our best calculation. This empirically derived structure differs significantly from that reported in ref 14 but is in excellent agreement (within 0.003 Å) with the structure based solely on high-level geometry optimizations.

Deviations between the present results and the bond lengths reported in ref 14 [0.007 Å for r(CC) and 0.005 Å for r(CH)] are clearly outside the range of any plausible error that might be associated with the calculated parameters. As both sets of data are based on the same set of experimental rotational constants, this suggests that incorrect assumptions have been made in the analysis of the data in ref 14.

On the other hand, the current set of parameters is in quite good agreement with the electron diffraction data, indicating that the analysis based on a diatomic-like model used in that work to account for stretching anharmonicity indeed has considerable merit. Furthermore, we note that the assumption made in ref 12 about the HCH angle, i.e., that α_z(HCH) = α_e(HCH), is more or less justified, as the computed value for α_z(HCH) of 114.53° (CCSD(T)/cc-pVQZ value) differs by less than 0.3° from the corresponding equilibrium value of 114.81°. However, we also note that the uncertainty associated with our parameters is significantly smaller than that of the electron diffraction data. The fit to the rotational constants yields a residual error of 0.064 MHz in the rotational constants for the final structure and also leads to essentially identical results (difference are about 0.000 01 Å and smaller) when the C_3H_6 data is not included. Similar results are also obtained when a lower level force field obtained at the SDQ-MBPT(4)/DZP level is used; the residual error is slightly larger, but differences in the geometrical parameters (0.0002 Å) are less than their estimated overall accuracy of 0.001 Å.

For completeness, Table 4 gives calculated harmonic frequencies for C_3H_6 (together with experimental fundamental frequencies from ref 10) and Table 5 summarizes the experimental and computed rotational constants for the various isotopomers of cyclopropane and also documents the computed vibrational corrections that were used to deduce the r_e structure for C_3H_6 from the experimental data.

As cyclopropane is an important prototype organic compound, it might be interesting to compare the obtained CC and CH bond distances to those of other simple hydrocarbons such as ethane, ethylene, and acetylene. The corresponding numbers obtained from CCSD(T)/cc-pVQZ calculations are gathered in Table 6. Most important, we note that the CC bond in cyclopropane is shorter than that in ethane by about 0.021 Å.[40] This is considerably less than the 0.04 Å often quoted in textbooks. Usually, this shortening of the CC bonds is attributed to the geometrical constraints of the three-membered ring, which lead to so-called “bent bonds”, the implications of which are discussed in the literature.[17,18] In this context, it is interesting to note that the CH bonds in cyclopropane (1.078 Å), which are clearly not bent, are also shortened when compared to ethane (1.088 Å). In fact, the obtained value for the CH bond length in cyclopropane is even shorter than the corresponding value for ethylene (1.080 Å). This CH bond shortening has also important implications, as the length of a bond is generally assumed to reflect its bond strength in the way that a shorter bond is also the stronger bond. Our results thus indicate that the CH bonds contribute to the “stabilization” of cyclopropane. Finally, we note that the HCH angle in cyclopropane (114.8°) also resembles more the corresponding angle in ethylene (117.1°) than that in ethane (107.7°).

IV. Conclusion

Using a two-pronged approach consisting of (a) highly accurate quantum chemical calculations and of (b) a reanalysis of experimental rotational constants based on computed vibra-

TABLE 4: Calculated Harmonic Frequencies (SDQ-MBPT(4)/cc-pVTZ) in Comparison with Experimental Fundamental Frequencies (in cm^{-1}) for Cyclopropane

symmetry	theory	exptl[a]	symmetry	theory	exptl[a]
E''	755.0	739.0	A_1'	1244.2	1188.0
A_2''	873.1	854.0	E'	1505.2	1437.7
E'	916.7	868.5	A_1'	1559.2	1479.0
E'	1084.6	1028.4	E'	3189.3	3024.4
A_2'	1116.4	1070.0	A_1'	3200.8	3038.0
A_1''	1182.4	1126.0	E''	3253.6	3082.0
E''	1237.5	1188.0	A_2''	3274.2	3101.7

[a] From ref 10.

TABLE 5: Calculated and Experimental Rotational Constants (in MHz) for Cyclopropane

	SDQ-MBPT(4)/ cc-pVTZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	exptl[a]
		(a) C_3H_6		
B_e	20 401.8	20 300.9	20 328.1	
C_e	12 753.6	12 690.9	12 715.5	
B_0	20 191.1	20 090.2[b]	20 117.3[b]	20 093.317(30)
C_0	12 603.6	12 540.9[b]	12 565.5[b]	12 522.3(90)
$B_e - B_0$	210.7			
$C_e - C_0$	150.0			
		(b) $C_3H_4D_2$		
A_e	19 127.6	19 032.8	19 055.5	
B_e	16 604.7	16 526.8	16 543.9	
C_e	11 580.4	11 525.6	11 545.9	
A_0	18 932.2	18 837.4[b]	18 860.1[b]	18 835.662(18)
B_0	16 448.3	16 370.4[b]	16 387.5[b]	16 370.2703(70)
C_0	11 451.7	11 396.9[b]	11 417.2[b]	11 409.2285(67)
$A_e - A_0$	195.4			
$B_e - B_0$	156.4			
$C_e - C_0$	128.7			

[a] Experimental values from ref 14. [b] Values obtained using vibrational corrections computed at the SDQ-MBPT(4)/cc-pVTZ level.

TABLE 6: Comparison of r_e Geometries of Simple Hydrocarbons (Bond Distances in Å, Angles in deg) As Obtained in CCSD(T)/cc-pVQZ Calculations

	r_e(CC)	r_e(CH)	α_e(HCH)
ethane	1.522	1.088	107.7
cyclopropane	1.502	1.078	114.8
ethylene	1.331	1.080	117.1
acetylene	1.204	1.061	

tional corrections, a long-standing controversy regarding the r_e structure of cyclopropane could be resolved. Excellent agreement is obtained in our approach between the structures obtained from high-level coupled-cluster calculations (CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ) and those obtained in the mixed experimental−theoretical approach to equilibrium geometries. The recommended parameters for cyclopropane of 1.5030(10) Å for r_e (CC), 1.0786(10) Å for r_e (CH), and 114.97(10)° for α_e(HCH) are in good agreement with an r_e geometry derived earlier on the basis of gas-phase electron diffraction data, although analysis of the rotational constants leads to significantly reduced error bars. Good agreement is also obtained between calculated and experimental r_g and r_z parameters. Our calculations, thus, validate the approach taken in ref 12 for the analysis of electron diffraction data. On the other hand, our results do not agree with those of ref 14. The discrepancy is traced to an inadequate treatment of the anharmonic corrections, as the r_z structure reported in ref 14 is consistent with our computational results.

Regarding the quantum chemical determination of the structure, it has to be concluded that accurate results are obtained for cyclopropane only if coupled-cluster methods with inclusion of triple excitations (i.e., CCSD(T)) are used together with large basis sets. The use of Dunning's hierarchy of correlation consistent basis sets represents a systematic approach to the basis set limit. Fairly good results are obtained for cyclopropane already with the cc-pVTZ set, while more reliable and accurate results require use of the larger cc-pVQZ set. Comparison with previous calculations reveals that a proper description of the geometry of cyclopropane necessitates use of higher-order angular momentum functions. Calculations without f-functions, for example, give the misleading impression that the r_e geometry of ref 14 is more accurate than that of YNFK. With respect to the electron correlation treatment, it should be noted that highly accurate results with remaining errors in the range of few thousandths of an angstrom can only be expected if the CCSD(T) approach is employed. Other standard approaches, i.e., MBPT(n) and CCSD, appear significantly less accurate.

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